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MECHANISM OF DOPING GALLIUM ARSENIDE WITH CARBON TETRACHLORIDE DURING ORGANOMETALLIC VAPOR-PHASE EPITAXY

by

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The rates of decomposition of carbon tetrachloride (CCl_4), triethylgallium (TEGa) and tertiarybutylarsine (TBAs), and the rate of GaAs film growth, were measured as a function of the process conditions during organometallic vapor-phase epitaxy. In addition, the reaction of CCl_4 with the GaAs(001) surface was monitored in ultrahigh vacuum using infrared spectroscopy, temperature-programmed desorption, and scanning tunneling microscopy. These experiments have revealed that CCl_4 adsorbs onto Ga sites, and decomposes by transferring chlorine ligands to other Ga atoms on the surface. Chlorine and gallium desorb from the surface as GaCl, while the carbon incorporates into the lattice. Triethylgallium is consumed by two competing reactions; GaAs film growth, and GaCl etching. Depending on the V/III and IV/III ratios and temperature, the etch rate can be high enough to prevent any GaAs deposition.

Key words: GaAs (001), carbon doping, carbon tetrachloride, OMVPE, TPD, STM

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INTRODUCTION

In the manufacture of GaAs/AlGaAs and InGaAs/InP heterojunction bipolar transistors (HBTs) by Organometallic Vapor-phase Epitaxy (OMVPE), heavy p-type doping of the GaAs or InGaAs base layer is necessary.[1-3] Carbon is the preferred p-type dopant due to its low diffusivity compared to zinc and beryllium.[4-7] Carbon tetrachloride (CCl$_4$) is an efficient OMVPE source for incorporating carbon into GaAs and InGaAs.[8-13] Under certain conditions, essentially all the carbon deposited from CCl$_4$ inserts into the acceptor sites of GaAs. However, CCl$_4$ also etches the film, resulting in InGaAs morphology that is unacceptable for use in electronic devices. The etch rate is much higher for indium than for gallium, making it difficult to precisely control the composition of the InGaAs film during growth and doping.

Previous studies have shown that the amount of carbon incorporated into GaAs increases with decreasing substrate temperature, decreasing V/III ratio, and increasing CCl$_4$ partial pressure.[12,14,15] Using isotopically labeled trimethylgallium, Buchan et al.[12] found that the CCl$_4$ is the source of the dopant in the film. These results indicate that the carbon incorporates via a heterogeneous reaction on the GaAs surface.[16] However, the mechanism of CCl$_4$ decomposition on GaAs(001) has not been identified.

In this paper, we report on our study of carbon incorporation into GaAs from CCl$_4$. The decomposition of CCl$_4$ and the other sources was monitored during the OMVPE of GaAs. In addition, the reaction of CCl$_4$ with the GaAs(001) surface was characterized in ultrahigh vacuum using surface science techniques. Our findings are described below.

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EXPERIMENTAL METHODS

The growth experiments were carried out in a low-pressure OMVPE reactor operated at 450 to 650 °C, 1.0 to 30.0 x 10^{-4} atm of TEGa, 1.0 to 50.0 x 10^{-4} atm of CCl$_4$, V/III ratios from 15 to 50, and a total pressure of 20 or 99 Torr. The arsenic source was TBAs, and the carrier gas was hydrogen obtained after passage through a palladium membrane. In the study of the reaction kinetics, the films were deposited on the walls of quartz tubes with an inside diameter of 4mm. Gallium Arsenide films prepared for the surface science experiments were grown on GaAs (001) substrates in a separate horizontal square duct reactor attached to the same flow system.

The consumption rates of the organometallic sources were determined by monitoring the gas-phase composition of the reactor feed and effluent with a Leybold Transpector 300 amu mass spectrometer and a BioRad FTS-7 infrared spectrometer. The infrared spectra of the gas streams were collected by passing them through a small flow cell, 17.7 cm long and 3.0 cm in diameter, that was sealed with KBr windows. Intense vibrational bands of TBAs, TEGa, and CCl$_4$ were detected at 2093, 544, and 793 cm^{-1}, respectively. [17,18] The bands were well resolved from each other, and provide a means of independently monitoring the consumption of each molecule during OMVPE. [19] The average growth rate of GaAs was determined to within 10% by weighing the quartz tube before and after the deposition of a film. Prior to the last weight measurement, the tube was rinsed with HCl to remove any GaCl$_x$ and As that accumulated downstream of the reaction zone during OMVPE.
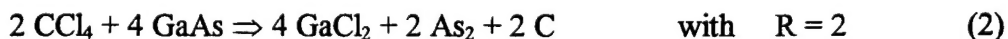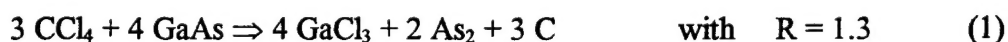
The surface science experiments were carried out in several vacuum chambers equipped with a Physical Electronics x-ray photoelectron spectrometer (XPS), a Balzers 200 amu mass spectrometer (MS), a Biorad FTS-40a infrared spectrometer (IR), a Princeton Instruments low-energy electron diffractometer (LEED), and a Park Autoprobe VP scanning tunneling microscope (STM). The base pressure in the chambers was 2 x 10^{-10} Torr. The vacuum chambers were connected to the OMVPE reactor through a sophisticated transfer system that allowed one to shuttle samples between the two locations without exposure to air. All of these experiments were carried out on 0.5 μm thick films grown at 1 μm/h on GaAs (001) substrates at 600 °C, 6.4 x 10^{-4} Torr of TEGa, a total pressure of 20 Torr, and a V/III ratio of 50.

Samples obtained from the OMVPE reactor were annealed for 10 min at 300, 450 and 580 °C to produce the c(4x4), c(2x8) and c(8x2) reconstructions, respectively. The c(2x8) surface was also exposed to 1000 Langmuirs AsH_3 at 300 °C (1Langmuir=1 x 10^{-6} Torr·s), and annealed another 10 min at this temperature. The different reconstructions were verified by LEED and by XPS. Next, the samples were held at either 30 or 200 °C and dosed with CCl_4 until the coverage reached a maximum. The dosages ranged from 150 to 2000 L. All filaments were turned off in the chamber during dosing to prevent the dissociation of the CCl_4 molecules. The relative coverage of CCl_4 was determined in the following way: The surface was dosed with hydrogen atoms and an infrared spectrum recorded of the adsorbate. By comparing the area of infrared bands for adsorbed hydrogen with and without the adsorbed CCl_4, the coverage of the latter species could be determined.[20]

After CCl₄ adsorption, the decomposition reaction was investigated by temperature-programmed desorption (TPD) and STM. In the case of TPD, the sample was placed in front of a quartz nozzle mounted on the end of the mass spectrometer. Then the sample was heated at 4 K/s while recording mass numbers corresponding to C, Cl, As, Ga, CCl₄, AsCl$_x$, and GaCl$_x$ species. Scanning-tunneling micrographs were obtained of the GaAs (001) surface after heating it to 450 °C to desorb all the chlorine. Tunneling was from filled states at a sample bias of -3.0 V.

RESULTS AND DISCUSSION

<u>OMVPE Growth</u>   The etching of GaAs by CCl₄ was examined first. In Figure 1 the dependence of the etch rate on the CCl₄ consumption rate over a temperature range between 400 and 500 °C is shown. The partial pressure of CCl₄ was held constant at 6.5 x 10⁻⁴ atm. The etch rate was determined by running the reaction for a given period of time, and then recording the mass of GaAs removed by weight over that period. This figure shows that the etch rate increases linearly with the CCl₄ consumption rate. The slope of the graph represents the number of Ga atoms etched per CCl₄ molecule reacted. There are three possible etching reactions:

$$3\ CCl_4 + 4\ GaAs \Rightarrow 4\ GaCl_3 + 2\ As_2 + 3\ C \qquad \text{with} \quad R = 1.3 \qquad (1)$$

$$2\ CCl_4 + 4\ GaAs \Rightarrow 4\ GaCl_2 + 2\ As_2 + 2\ C \qquad \text{with} \quad R = 2 \qquad (2)$$

$$CCl_4 + 4\ GaAs \Rightarrow 4\ GaCl + 2\ As_2 + \quad C \qquad \text{with} \quad R = 4 \qquad (3)$$

In these mechanisms, R is the molar ratio of GaAs to CCl₄. In Figure 1, the slopes of the lines for each value of R are shown. It can be seen that the data follows R = 1.3, which indicates that GaCl₃ is produced under these conditions. The activation energy for GaAs

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etching with CCl₄ was measured to be 17 kcal/mol, between 350 and 550 °C. It should be noted that the addition of TBAs to the feed gas completely inhibits GaAs etching below 450 °C.

[Insert Figure 1]

Figure 2 shows the dependence of the consumption rates of CCl₄ and TEGa on the TEGa partial pressure at 450 °C. The consumption rates were calculated from infrared measurements. In this experiment, a GaAs film was grown, the TBAs flow was turned off, and CCl₄ and TEGa were fed together through the tube. The CCl₄ partial pressure was kept constant at 6.5×10^{-4} atm. The conversion of both sources during the pyrolysis reactions increase with the TEGa partial pressure. Under these conditions, there is no etching of the GaAs film. The ratio of TEGa consumed to CCl₄ consumed is approximately four, indicating that GaCl is formed according to reaction (3) above.

[Insert Figure 2]

In Figure 3, the consumption rates of TBAs, TEGa and CCl₄ are plotted versus the CCl₄ partial pressure for OMVPE of GaAs at 450 °C. The TEGa partial pressure was 6.5×10^{-4} atm, and the V/III ratio was 15. The CCl₄ reaction rate is directly proportional to the CCl₄ partial pressure. By contrast, the TBAs consumption rate decreases slightly, while the TEGa consumption rate increases slightly with the amount of CCl₄ fed. Assuming no etching occurs, then the solid line in the figure represents the estimated Ga consumed by the film, i.e. GaAs growth rate, as calculated from the difference between the TEGa consumption rate and the GaCl production rate (which equals 4x the CCl₄ conversion rate). This curve coincides well with the growth rates determined by weighing

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the tubes after the run. At the highest CCl_4 partial pressures examined in the experiment, the GaAs growth rate is essentially zero.

[Insert Figure 3]

The results presented above indicate that two different reactions occur depending on whether the GaAs film is etched, or adsorbed Ga from TEGa is etched. In the former case, the etch product is $GaCl_3$, while in the latter case, it is GaCl. During OMVPE of GaAs, adsorbed Ga reacts with chlorine species to produce GaCl. This reaction effectively reduces the amount of adsorbed Ga which incorporates into the growing film.

No other chlorinated hydrocarbons were detected in the exit stream of the OMVPE reactor other than CCl_4. Some of the carbon from CCl_4 could have been converted into CH_4 or other hydrocarbons, since this would have been difficult to distinguish from the hydrocarbons produced from the other organometallic sources. Nevertheless, assuming all the CCl_4 consumed is converted into carbon, then for the growth conditions used to generate Figure 3, the mole ratio of carbon to GaAs produced varies from 0.05 at 1×10^{-4} atm CCl_4 to 4.0 at 3×10^{-3} atm CCl_4. These ratios are much higher than what one would achieve for acceptor doping of GaAs. It is likely that much of the carbon produced from CCl_4 precipitated out as a separate phase from the GaAs. Further experiments are underway to clarify this point.

Surface Reactions   Table 1 summarizes the saturation coverages of CCl_4 on three reconstructions of GaAs (001). The amount taken up is proportional to Ga coverage, and decreases to zero on the c(4x4) which has no gallium sites. By raising the substrate temperature from 30 to 200 °C, the saturation coverage goes up by a factor of three. At

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200 °C on the c(8x2) reconstruction, all the adsorption sites are occupied, including the arsenic sites. These results indicate that CCl_4 adsorbs onto exposed Ga atoms, and dissociates with the transfer of several of its chlorine ligands to neighboring As and Ga atoms. Due to the enhanced mobility of chlorine at 200 °C, the atoms can pack together more efficiently and achieve a higher coverage.

Figure 4 shows TPD spectra for CCl_4 adsorbed on both the c(2x8) and c(8x2) reconstructions. These spectra were taken after dosing the CCl_4 onto the surfaces at 200 °C. On the c(2x8), only Cl atom desorption is observed. No mass fragments due to CCl_x, $AsCl_x$, or $GaCl_x$ species were detected. Evidently, some of the adsorbed CCl_4 decomposes on this surface by desorbing Cl or Cl_2 back into the gas. After the TPD experiment on the c(2x8), the surface reconstruction is unchanged. By contrast, on the Ga-rich c(8x2) reconstruction, Ga, GaCl and Cl desorb in a single peak centered at 425 °C. The three peaks are due to the mass fragmentation pattern of GaCl. No $AsCl_x$ or CCl_x species are detected. After heating, the LEED pattern changes, and the XPS spectra confirm that the GaAs (001) surface has become more arsenic rich. These results are consistent with what we observe during OMVPE with CCl_4. Namely, the CCl_4 etches adsorbed gallium from the surface as gallium monochloride.

Figure 5a is a scanning tunneling micrograph of the GaAs (001) surface obtained after adsorbing CCl_4 on the c(8x2) reconstruction at 200 °C and annealing the sample at 450 °C for 15 min to desorb GaCl. In the center of the image is a rough region of the surface that varies in contrast from black to white. Within this area are rows of grey and white chains that exhibit a periodicity of 8 Å parallel to the chain and 16 Å perpendicular to it. These chains are due to the 3 As dimers of the (2x4)/c(2x8) unit cell. Figure 5b is a

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model of this structure. The Ga coverage on this reconstruction is 0.25. The region in the center of the image is obviously an etch pit produced upon the desorption of GaCl. The distance from the top of the terrace to the bottom of the pit is approximately 5 As terminated layers, or ~13.6 Å. Large scale STM images reveal that these etch pits crisscross the terraces on the surface, and occupy about 10% of the total area.

[Insert Figure 5]

The flat terraces surrounding the etch pit in Fig.5a exhibit a (3x2) reconstruction. Close inspection of the image reveals that the terraces contain a series of light grey rows which are perpendicular to the (2x4) chains. The row spacing is 12 Å (x3). A LEED picture recorded of this surface also shows a bright (3x2) pattern. A model of the (3x2) reconstruction is displayed in Fig. 5c. It consists of single rows of Ga dimers in the top layer separated by single rows of Ga dimers in the second layer below. One carbon atom is shown substituted into an As lattice site underneath the Ga dimer. This carbon atom is needed to make up for the deficit of one electron per (3x2) unit cell. It should be noted that on an undoped GaAs (001) surface, the (3x2) reconstruction can be produced; however, this reconstruction contains a series of line defects which expose arsenic in the underlying layers.[21] The line defects provide the extra electrons needed for charge neutrality. By contrast, carbon liberated from CCl_4 decomposition can substitute into the arsenic sites, and stabilize the (3x2) reconstruction without generating line defects. Thus, the STM image reveals the process by which carbon may incorporate into the lattice and acceptor dope the GaAs film.

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CONCLUSIONS

Carbon tetrachloride decomposes on gallium sites to form adsorbed carbon and chlorine. The chlorine migrates to nearby As and Ga sites. During OMVPE, and annealing of Ga-rich surfaces, the chlorine desorbs along with gallium as GaCl. On the other hand, the carbon, stripped of its Cl ligands, incorporates into the lattice. Our model predicts that the carbon incorporates into an As lattice site.

Under OMVPE conditions, the growth rate is reduced by the amount of adsorbed Ga from TEGa that is converted to GaCl by the CCl_4.

ACKNOWLEDGEMENTS

REFERENCES

1. H. Kroemer, *Proc. IEEE* 70, 13 (1982).

2. G.W. Wang, *IEEE Electron Device Lett.* 11, 241 (1990).

3. S.A. Stockman, A.W. Hanson, S.M. Lichtenthal, M.T. Fresina, G.E. Hofler, K.C. Hsieh, and G.E. Stillman, *J. Electron. Mater.* 21, 1111 (1992).

4. D.L. Miller, and P.M. Asbeck, *J. Appl. Phys.* 28, 1816 (1985).

5. T.F. Keuch, M.A. Tischler, P.-J. Wang, G. Scilla, R. Potemski, and F. Cardone, *Appl. Phys. Lett.* 53, 1317 (1988).

6. P. Enquist, J.A. Hutchby, and T.J. de Lyon, *J. Appl. Phys.* 63, 4485 (1988).

7. M. Wada, M. Seko, K. Sakakibara, and Y. Sekiguchi, *Jpn. J. Appl. Phys.* 28, L1700 (1989).

8. B.T. Cunningham, M.A. Haase, M.J. McCollum, J.E. Baker, and G.E. Stillman, *Appl. Phys. Lett.* 54, 1905, (1989).

9. N.I. Buchan, T.F. Keuch, G. Scilla, F. Cardone, and R. Potemski, *J. Electron. Mater.* 19, 277 (1990).

10. B.T. Cunningham, G.E. Stillman, and G.S. Jackson, *Appl. Phys. Lett.* 56, 361 (1990).

11. M.C. Hanna, Z.H. Lu, E.W. Mao, T. McCormick, E.G. Oh, A. Majerfeld, and D.M. Szmyd, *J. Crystal Growth* 107, 279 (1991).

12. N.I. Buchan, T.F. Keuch, G. Scilla and G. Cardone, *J. Crystal Growth* 110, 405 (1991).

13. S. Stockman, A. Hanson, C. Coloumb, M. Fresina, J. Baker and J. Stillman, *J. Electron. Mat.* 23, 791 (1994).

14. B.T. Cunningham, J.E. Baker, and G.E. Stillman, *J. Electron. Mater.* 19, 331 (1990).

15. M.C. Hanna, Z.H. Lu, and A. Majerfeld, *Appl. Phys. Lett.* 58, 164 (1991).

16. P.A. Goulding and M.E. Pemble, *Surf. Sci. Lett.* 247, L201 (1991).

17. L.J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1956.

18. E. Maslowsky Jr., *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, 1977.

19. K.J. Wilkerson, M.J. Kappers, and R.F. Hicks, *J. Phys. Chem.* A101, 2451 (1990).

20. H. Qi, P.F. Gee, and R.F. Hicks, *Phys. Rev. Lett.* 72, 250 (1994).

21. Li, S. Gan, B.K. Han, and R.F. Hicks, to be published.

Table 1: Carbon tetrachloride uptake on different GaAs(001) reconstructions at 30 and 200 °C.

GaAs reconstruction	Ga coverage	CCl$_4$ saturation coverage (ML)	
		30 °C	200 °C
c(4x4)	0.00	<0.05	0.05
c(2x8)	0.25	0.11	0.30
c(8x2)	0.75	0.29	0.93

Figure 1: The dependence of the GaAs etching rate on the CCl_4 consumption rate at different temperatures (400<T<500 °C) in H_2 carrier gas.

Figure 2: The dependence of the consumption rates of CCl_4 and TEGa on the TEGa partial pressure at 450 °C in H_2 carrier gas.

Figure 3: The dependence of the consumption rates of CCl_4, TBAs and TEGa on the CCl_4 partial pressure during GaAs OMVPE at 450 °C. The estimated growth rate is shown as a solid line, and the growth rate determined gravimetrically is plotted as diamonds ($\Diamond$).

Figure 4: Temperature programmed desorption spectra of the c(2x8) and c(8x2) Cl^+ (m/e = 35), Ga^+ (m/e = 69) and $GaCl^+$ (m/e = 104) from reconstructions of GaAs (001) after CCl_4 adsorption at 200 °C.

Figure 5: (a) Scanning tunneling micrograph of the GaAs (001) surface after CCl_4 adsorption on the c(8x2) reconstruction at 200 °C and annealing at 450 °C. The image size is 350 Å x 350 Å; (b) Structural model for the (2x4)/c(2x8) reconstruction; and (c) Structural model for the (3x2) reconstruction.
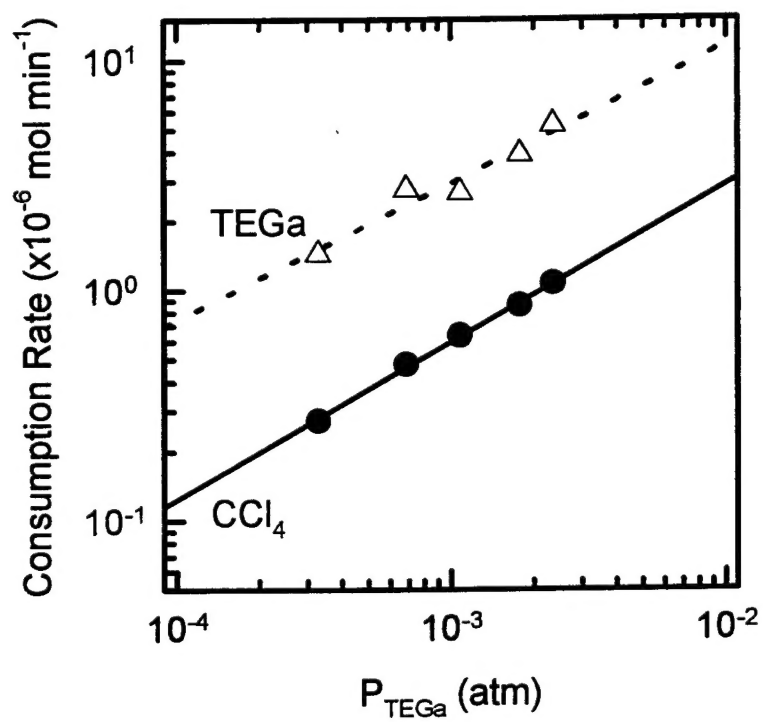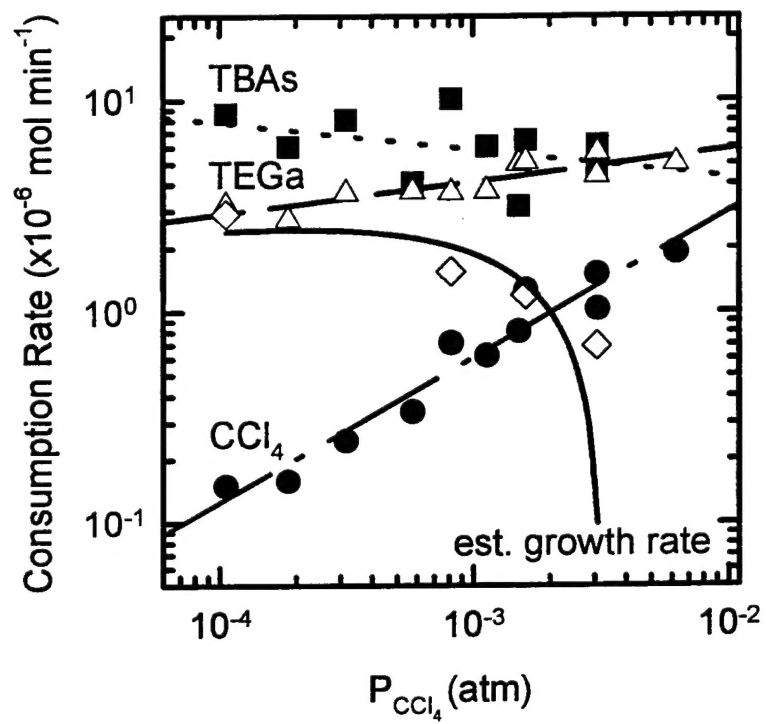
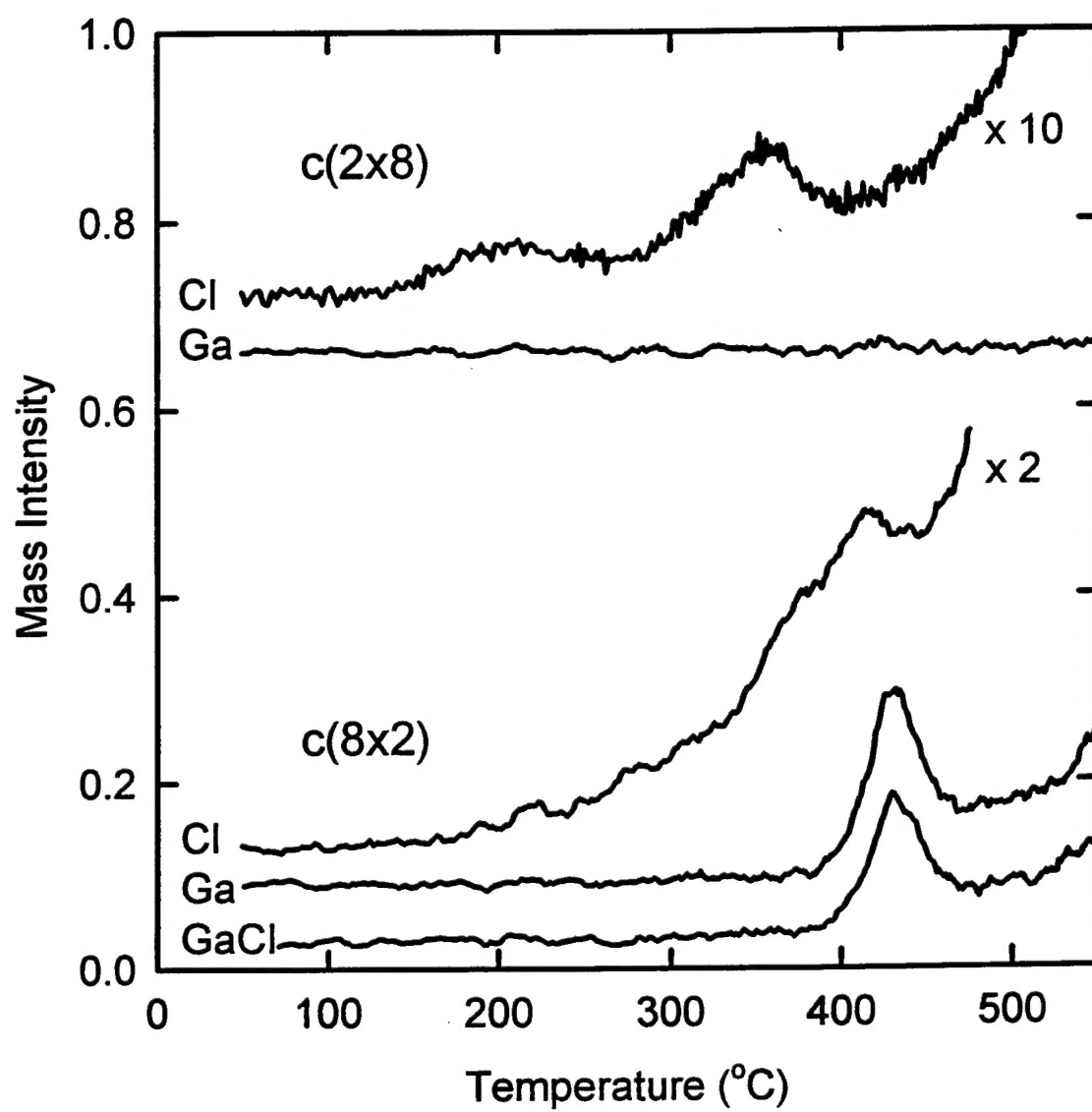# Warddrip et al.

Figure 1
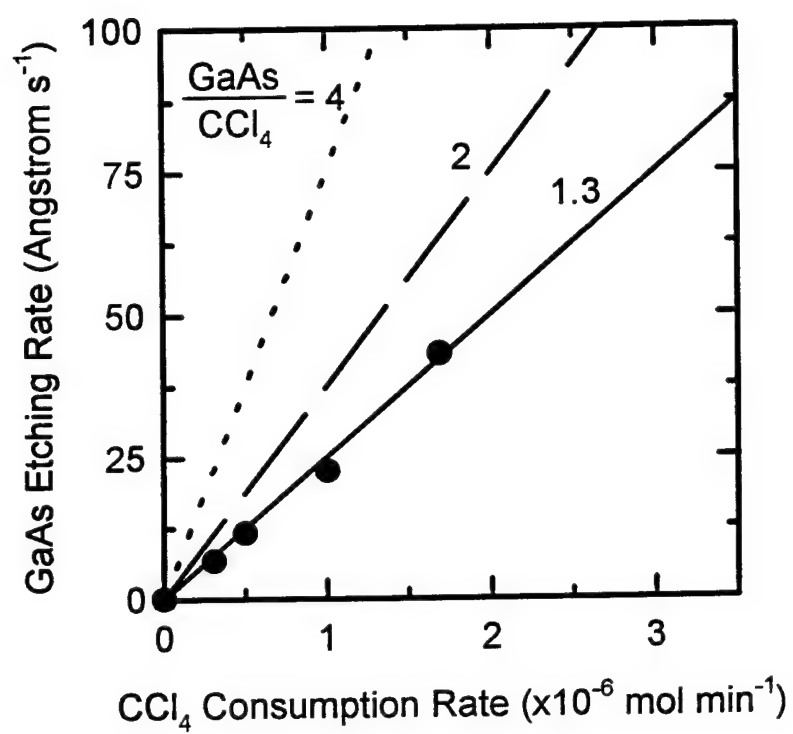
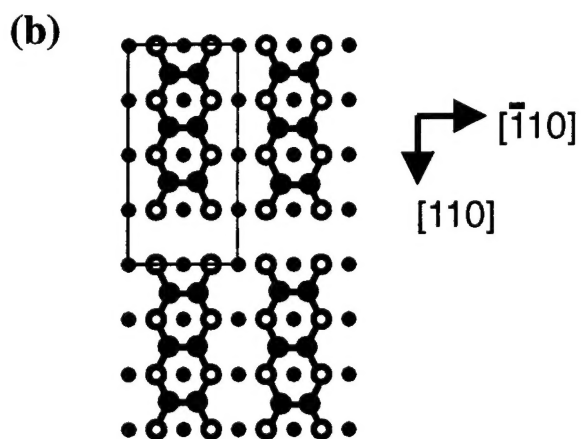# Warddrip et al.

Figure 2

Warddrip et al.

Figure 3

(a)

[¯110]
[110]

(b)

[¯110]
[110]

(2x4)/c(2x8)

(c)
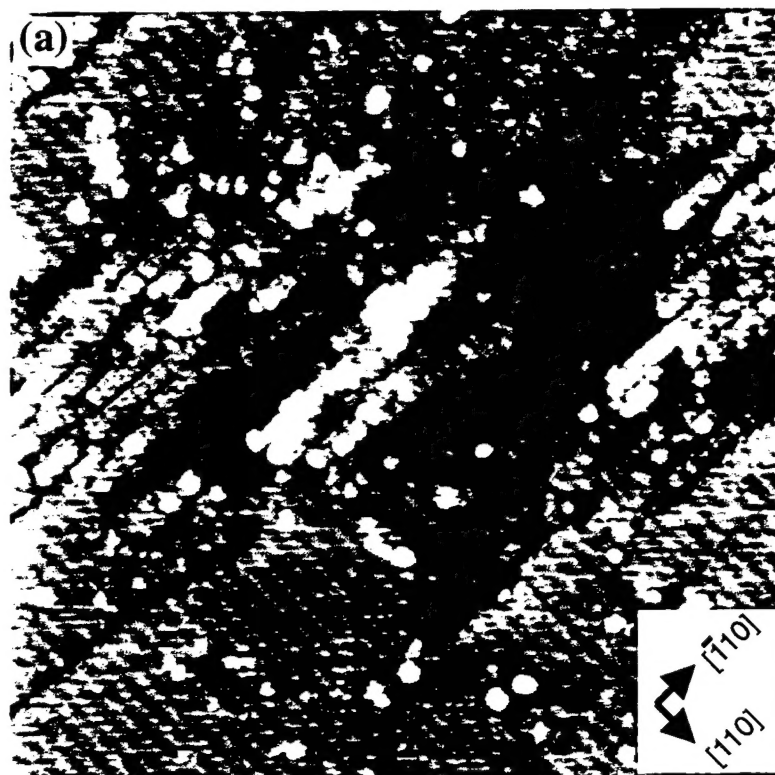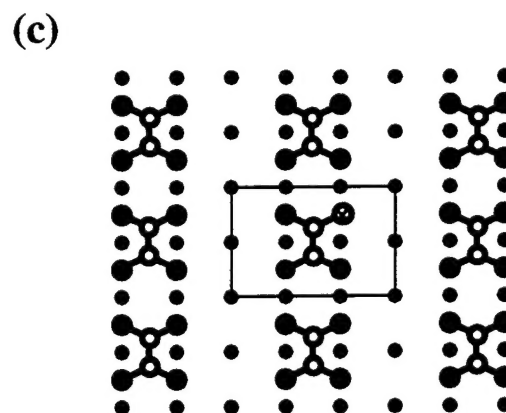
(3x2)

○ First layer Ga
● First layer As

◐ Second layer Ga(As)
⊗ Substitution C